AD-A058 052   SRI INTERNATIONAL, MENLO PARK CA   F/G 11/6
                A STUDY TO DETERMINE THE MECHANISMS OF CORROSION OF COPPER ALLO--ETC(U)
                AUG 78   B C SYRETT, S S WING, D D MACDONALD   N00014-77-C-0046

UNCLASSIFIED   NL

| OF |
ADA
058052

END
DATE
FILMED

10 -78

DDC

SRI International

LEVEL II ①

⑪ 1 August 1978 ⑫ 8p.

SC

⑨ Quarterly Progress Report, No. 6,
Covering the Period 1 May 1978 to 31 July 1978

⑥ A STUDY TO DETERMINE THE MECHANISMS OF CORROSION OF
COPPER ALLOYS IN SULFIDE-POLLUTED SEAWATER.

⑩ By: Barry C. Syrett, Sharon S. Wing and
Digby D. Macdonald

Prepared for:

OFFICE OF NAVAL RESEARCH
Materials Sciences Division
800 North Quincy Street
Arlington, Virginia 22217

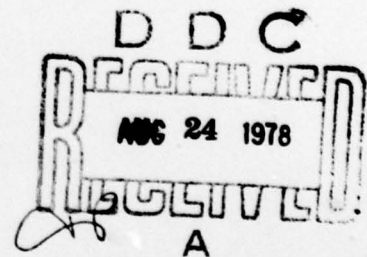Attention: Dr. Philip A. Clarkin, Code 471
Director, Metallurgy Program

⑮ Contract No. N00014-77-C-0046
SRI Project No. PYU 6077

Approved:

R. W. Bartlett, Director
Materials Research Center

D D C
RECEIVED
AUG 24 1978
A

SRI International

78 08 21 089

410 281   LB

SIXTH QUARTERLY PROGRESS REPORT

As part of ~~our~~ *a* continuing program to determine the mechanisms of
corrosion of copper-nickel alloys in sulfide-polluted seawater, ~~we have~~ *the investigators*
conducted flow loop experiments, using unpolluted aerated seawater, and
also rotating cylinder experiments, using seawater contaminated with
various sulfur-containing species. The series of flow loop experiments
were performed to obtain baseline corrosion rates for copper-nickel alloys
under carefully controlled hydrodynamic and mass transfer conditions.
This loop will also be used later in the program to measure corrosion
rates in seawater polluted with sulfur-containing species. The series of
rotating cylinder experiments were performed to rapidly determine the
relative corrosivities of seawater containing sulfide, oxygen, or sulfide
oxidation products (including elemental sulfur). The latter tests will
define the most relevant seawater pollutants to be used in subsequent
flow loop experiments.

Neither series of tests has been completed yet, but ~~our~~ progress is
summarized ~~below,~~ together with preliminary conclusions.

Flow Loop Experiments

The effect of velocity on the corrosion mechanism and on the corro-
sion rate of 90:10 Cu:Ni and 70:30 Cu:Ni has been investigated using
aerated, sulfide-free seawater flowing in the test loop described in
Quarterly Progress Report No. 5. At average seawater velocities of 1, 2,
and 3 m/s, the corrosion rates of both alloys increased steadily with
increasing velocity, as indicated by weight-loss measurements, by polari-
zation resistance (R_p) measurements (after a 10-day exposure), and by

measurement of the areas under the $1/R_p$ versus time curves. Furthermore, the 90:10 Cu:Ni alloy corroded more rapidly than the higher nickel alloy under these conditions. However, at a velocity of 4 m/s, the instantaneous corrosion rate $(1/R_p)$ of 90:10 Cu:Ni after a 10-day exposure was significantly lower than that of 70:30 Cu:Ni, although weight-loss measurements indicated that the integrated corrosion rates over the 10-day period were similar for both alloys. The significance of this reversal in corrosion susceptibility at 4 m/s is currently being investigated. It is likely that an additional test (probably at a velocity of 5 m/s) will be performed using aerated seawater to establish a better data base for subsequent flow tests in polluted seawater.

Rotating Cylinder Experiments

The effect on corrosivity of various sulfur-containing species thought to exist in polluted seawater was assessed using the rotating-cylinder apparatus described in Quarterly Progress Report No. 5. These rapid screening tests were performed in seawater containing:

(1) 6.67 ppm total sulfide (no oxygen).

(2) 6.80 ppm colloidal sulfur (no oxygen).

(3) 3.30 ppm oxygen plus 3.42 ppm total sulfide.

(4) 3.39 ppm sulfide plus 3.35 ppm colloidal sulfur (no oxygen).

Control tests were performed in aerated seawater (6.6 ppm oxygen). In each rotating-cylinder test, the total initial concentration of active species (oxygen/sulfide/sulfur) was in the range 6.6 to 6.8 ppm. These tests were performed in closed environmental chambers at a rotational speed of 400 rpm and the corrosion rates of 90:10 Cu:Ni and 70:30 Cu:Ni cylindrical specimens were monitored for about 29 hours using the linear

2

polarization and potential step techniques. Since oxygen, sulfur, and sulfide were not replenished during the test, the level of each of these species in seawater dropped as it reacted with the copper alloys. In addition, in seawater doped with colloidal sulfur, surface charge effects caused a significant portion of the sulfur to cling to glass and plastic components of the apparatus, and to the electrode surfaces. Nevertheless, measurement of the rate of decrease of oxygen and sulfur-containing species provided useful information on the rates of the reactions occurring on the copper alloy surfaces.

Sulfide Alone and Oxygen Alone

The sulfide content of the deoxygenated, sulfide-polluted seawater, and the oxygen content of the aerated, unpolluted seawater decreased during the first five hours but thereafter, remained relatively constant; this observation suggests that the average corrosion rate for the two alloys was high initially but that it dropped to a significantly lower value after a few hours. The polarization-resistance data were consistent with this suggestion: although the corrosion rate for 90:10 Cu:Ni did not decrease significantly after five hours of testing, the 70:30 Cu:Ni alloy showed a significant decrease in corrosion rate after about five hours in both of these environments.

Sulfur Alone and Sulfide-Plus-Oxygen

In contrast to the small change in the chemical composition of the sulfide-polluted and the aerated environments, rapid and relatively large changes in chemistry were noted in the seawater containing sulfur, and in the seawater containing both sulfide and oxygen. Tests performed in the latter two environments were predicted to have at least a few

3

common characteristics because dissolved sulfide can be oxidized fairly rapidly[1] by dissolved oxygen to form sulfur[2] (and other oxidation products). In fact, although there were no obvious visible signs of sulfur formation in the sulfide-plus-oxygen environment, the corrosion rate versus time curves for each alloy in each of these environments were very similar. Specifically, corrosion rates increased initially, showed a maximum after 1 to 3 hours, and decreased monotonically thereafter; corrosion rates at the end of the test period were always about 30% of the peak value. However, one characteristic of the test in seawater containing only sulfur was unique: the polarization resistance values for both copper-nickel alloys were very similar at any instant over the entire test period. In the sulfide-plus-oxygen environment and in the other three environments considered, the 70:30 Cu:Ni alloy exhibited higher polarization resistance values (lower corrosion rates) than the 90:10 Cu:Ni alloy. Thus, the generally superior corrosion resistance of the 70:30 Cu:Ni alloy appeared to have been lost in seawater containing sulfur alone. Popplewell has also reported[3] that the high nickel alloy lost its superiority over the 90:10 Cu:Ni alloy when exposed alternatively to flowing aerated 3.4% NaCl solution and to the same solution containing 10 ppm sulfide. It is possible that sulfur, formed by the homogeneous oxidation of dissolved sulfide, played an important role in the corrosion mechanism in Popplewell's tests too. In the near future, we will define more precisely the sulfide oxidation products that form and the rates of formation in our sulfide-plus-

---

[1]H.G. Ostlund and J. Alexander, J. of Geophys. Res., 68, p. 399 (1963).

[2]M. Avrahami and R. M. Golding, J. Chem. Soc. (A), 34, p. 647 (1968).

[3]J. M. Popplewell, "Marine Corrosion of Copper Alloys: An Overview." Paper No. 21 at Corrosion/78, National Association of Corrosion Engineers Annual Conference, Houston, Texas (March 1978).

oxygen environment. Such information will greatly facilitate an explanation of the corrosion mechanisms operating in this naturally occurring environment.

Sulfide Alone and Sulfide-Plus-Sulfur

The rate at which the sulfide level dropped in the sulfide-plus-sulfur environment was much more rapid than in seawater containing only sulfide. This suggests that one or both copper-nickel alloys corrode more rapidly when sulfur is present with sulfide than when sulfide is present alone. The polarization resistance data, while not providing irrefutable evidence, were not inconsistent with this suggestion. Moreover, whereas the corrosion rate either remained constant (90:10 Cu:Ni) or decreased with time (70:30 Cu:Ni) in seawater containing only sulfide, the corrosion rate of both alloys increased with time after the first two hours of testing in the copresence of sulfide and sulfur. A scanning electron microscopic examination indicated that the specimens exhibiting an increasing corrosion rate had produced more porous and less perfect surface films than those produced on specimens showing constant or decreasing corrosion rates. Such differences in morphology are consistent with the observed corrosion rate responses.

Corrosion Rates

The reciprocal of the polarization resistance, $1/R_p$ is directly proportional to the corrosion current (and corrosion rate) through the Stern-Geary relationship, and the constant of proportionality is a function only of the anodic and cathodic Tafel slopes. It is quite likely that the Tafel slopes were different for each of the systems we studied, so $1/R_p$ values obtained in one system were unlikely to be related to corrosion rates in the same manner as in another system.

5

Unfortunately, the Tafel slopes for the systems we studied are currently unknown, so the proportionality constants cannot be calculated with accuracy. However, an estimate of each constant can be made by assuming reasonable Tafel slopes and the corrosion current can then be calculated by multiplying the $1/R_p$ value by the relevant constant. A corrosion current calculated in this way is probably in error by no more than a factor of three or four. Such estimates allowed us to make a preliminary comparison of corrosion rates in the five seawater environments. In the relatively short period of our tests, it appears that there is no clear-cut evidence that one environment is considerably more corrosive than another. Conversely, it is clear that deaerated seawater, which is non-corrosive towards copper alloys in the absence of sulfur-containing species, is corrosive in the presence of dissolved sulfide, or colloidal sulfur, or both of these species. Detailed descriptions of the various corrosion mechanisms involved will be contained in the Annual Report to ONR.

To support and extend these preliminary screening tests additional rotating cylinder experiments are planned in which the level of active species is maintained almost constant for the duration of the test. In addition, electrical connection to the cylinders will be made mechanically, rather than by soldering, to facilitate posttest weight-loss measurements. These additional tests will more precisely define the aggressive environmental conditions that will be used subsequently in the flow loop experiments.

Future Work

In summary, work on this project is progressing well, but we foresee the need to depart slightly from our proposed work plan (SRI International Proposal No. PYU 77-296) so that we may more readily achieve our objective of determining corrosion mechanisms in polluted seawater. We now propose

to extend the rotating cylinder experiments and also to perform a series of more detailed chemical analyses of seawater initially containing both sulfide and oxygen. Details of the proposed changes in work plan will be discussed in the near future with Dr. P. Clarkin (ONR).